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# EFFECT OF ANNEALED TEMPERATURE ON $NO_2$ GAS-SENSING PERFORMANCES OF $SnO_2$ NANOWIRE SENSORS

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**ABSTRACT**

$NO_2$ gas is a highly toxic gas and emitted from vehicles such as motocycles and internal engine transportations. It is one of the major reasons which cause air pollution in recent years, especially in big cities. Therefore, the development of $NO_2$ gas sensor for environmental monitoring has been gained research attention in the global. In this work, we report a simple and effective method to prepare $SnO_2$ nanowire gas sensors. The $SnO_2$ nanowires were directly grown on the unplosihed $Al_2O_3$ substrate equipped with a pair of Pt-electrodes. The morphology and microstructure of as-grown nanowires have been investigated via X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and transimission electron microscopy (TEM). The results indicated that the diameters and lengths of nanowires are about 60 – 100 nm and tens of µm, respectively. The gas-sensing performance of the $SnO_2$ nanowires sensors annealed at different temperatures have also investigated. The results revealed that the annealed temperatures of 400 °C and 500 °C do not affected on gas-sensing performance of $SnO_2$ nanowires sensors, while the annealed temperature of 600 °C results in strong decrease in $NO_2$ gas response as compared with as-grown $SnO_2$ nanowires sensor.

*Keywords:* $SnO_2$, $NO_2$, gas sensors, nanowires.

## 1. INTRODUCTION

Recent years, the rapid growth of the number of vehicles in operation, the air pollutants emitted from these vehicles have contributed to air pollution, especially in large cities. The levels of pollution by CO, $NO_2$, $SO_2$, $CO_2$ and $NH_3$ have increased many times the level allowed standards. Therefore, the development of gas sensors for the detection of such gases has attracted considerable interest in recent years [1]. Many metal oxide semiconductors including ZnO, $SnO_2$, $WO_3$ and $In_2O_3$ have been applied for gas sensors [2]. Among them, $SnO_2$ has been emerged as one of the most promising candidate due to its high sensitivity [3], good selectivity [4] and low cost [5]. Many techniques for growing $SnO_2$ nanowires have been successfully developed such as hydrothermal growth [6], pulse laser deposition [7], sol-gel [8], and chemical vapor deposition [9]. The most commontly used method for fabricating $SnO_2$ nanowires is tube furnace type thermal evaporation due to the simplicity, high-quality nanowires and low cost of this approach.

Nitrogen dioxide ($NO_2$) is highly harmful as an environmental pollutant which causes photochemical smog and acid rain. For environmental and safety reasons, gas sensors are required for monitoring concentration of $NO_2$ gas in air. In this work, we report the synthesis and physical characterizations of $SnO_2$ nanowires produced using thermal evaporation technique for gas sensor application. Besides, the gas-sensing performance of the $SnO_2$ nanowire sensors annealed at different temperatures have also investigated. The results show that the sensors exhibit good gas sensing performance to $NO_2$ gas. Especially, the sensors can detect $NO_2$ gas at low concentration range (ppb).

## 2. EXPERIMENTAL

The $SnO_2$ nanowires were grown by a chemical vapor depositon (CVD) system as shown in Figure 1. Pure Sn powder (Merck, 99.8 %) was placed in an alumina boat as the evaporation materials sources. The substrates with a previously deposited 10 nm Au catalyst layer were placed approximately 2–3 cm from the sources on both sides (up-stream and down-stream). The growth process was divided into two steps.

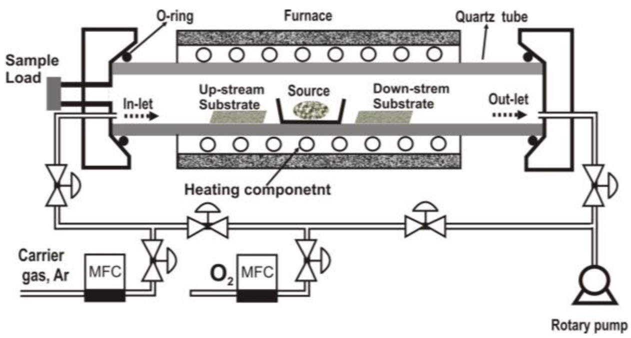


*Figure 1.* Schematic diagram of CVD system to synthesis $SnO_2$ nanowires.

Initially, the quartz tube was evacuated to $10^{-2}$ Torr and purged several times with Ar gas (99.999 %). Subsequently, the quartz tube was evacuated to 10 Torr again, and the furnace temperature was increased from room-temperature to 750 °C in 20 minutes. After the furnace temperature reached the synthesized temperatures, oxygen gas was added to the quartz tube at a flow rate of 0.5 sccm, and the growth process was maintained for another 30 minutes. The as-synthesized $SnO_2$ nanowires were analyzed by X-Ray Diffraction (XRD, D8 Advance, Brucker, Germany), Field Emission Scanning Electron Microscopy (FE-SEM, S4800, Hitachi) and Transmission Electron Microscopy (TEM, JEM-100CX).

The gas-sensing properties were then measured with a standard flow rate of 400 sccm for both dry air balance and analytic gases. During sensing measurement, resistance of the sensors was continuously measured using a Keithley 2700 instrument interfaced with a computer while the dried air and analytic gases were switched on/off in each cycle. Sensors response was defined as $S = R_g/R_a$, where $R_g$ and $R_a$ are resistances of sensor in target gas and dry air, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1. Material characterizations

Figure 2(a) shows the XRD pattern of $SnO_2$ nanowires. It can be seen from the diffraction patterns that there are typical peaks for tetragonal tin dioxide, which are (110), (101), and (211) planes. All the peaks are well indexed to the tetragonal structure with lattice constants a = 4.73Å nm, c = 3.18 Å, which are in good agreement with those in the standard data card (JCPDS Card No. 77–0452).

The morphologies of the $SnO_2$ fabricated by thermal evaporation were characterized by FE-SEM and TEM images and the results were indicated in Figure 3(b-d). It can be seen that the $SnO_2$ nanowires were successfully synthesized at the temperature of 750°C on $Al_2O_3$ substrate (Figure 3b). The high magnification of FESEM and TEM images of the $SnO_2$ nanowires (Figures 3c and 3d) are revealed a smoothness and uniformity along the surface of the wire axis. Uniform $SnO_2$ nanowires were produced on a very large area of the substrate. The average diameters and lengths of the $SnO_2$ nanowires ranged from 60 to 100 nm, and from 50 to 150 µm, respectively.

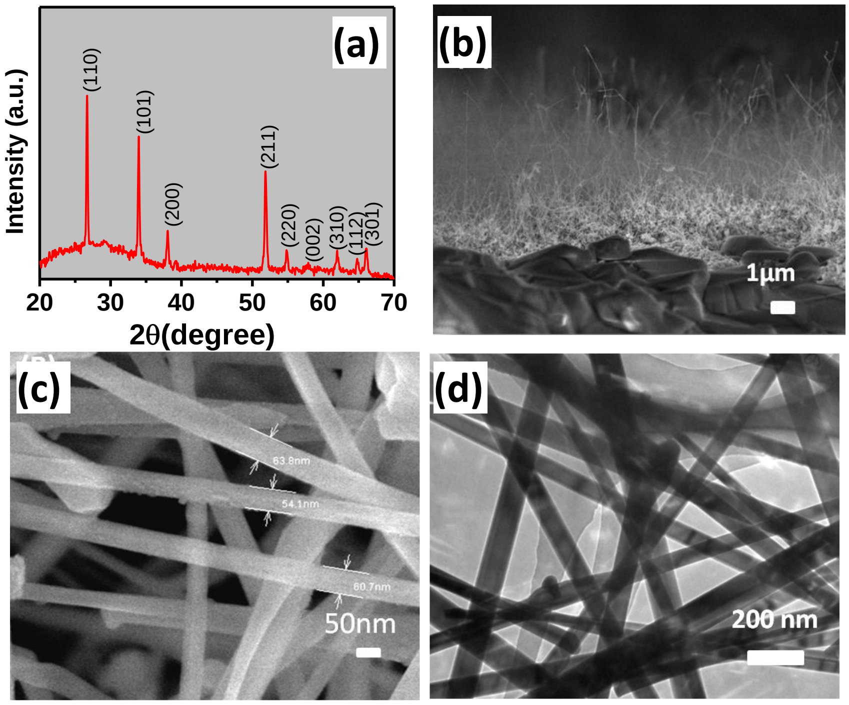


*Figure 2.* Materials charatcerizations: (a) XRD pattern; (b,c) FE-SEM and (d) TEM image of the $SnO_2$ nanowires fabricated by thermal evaporation.

### 3.2. Gas sensing properties

In order to investigate gas-sensing performance of the $SnO_2$ nanowire sensors, a dynamic gas-sensing test was performed. The $NO_2$ gas-sensing properties of as-grown $SnO_2$ nanowire sensor are summarized in Figure 3. A good response-recovery characteristic was obtained under sensing temperature range of 150 – 250°C and 0.1-1 ppm $NO_2$ gas. As can be seen, the sensor could detect $NO_2$ gas at low concentrations (su-ppm). However, the highest response was obtained at working temperature of 150 °C, in which the sensor resistance increased rapidly upon exposure to target gas and reached saturation within few minutes. The response ($R_g/R_a$) increased from about 10 to 160 when target gas concentration increased from 100 to 1000 ppb. The resistance of sensors exhibited a upward trend when exposure to $NO_2$ gas, because $SnO_2$ material is known as an *n*-type semiconductor with free electrons as carriers due to the vacancy of oxygen, while $NO_2$ is a oxidation gas. Thus, when $NO_2$ was adsorbed on the surface, the $NO_2$ molecules accepted the electron from the tin oxide nanowires, decreased the carrier density, and resulted in the increase sensors' resistance [10].

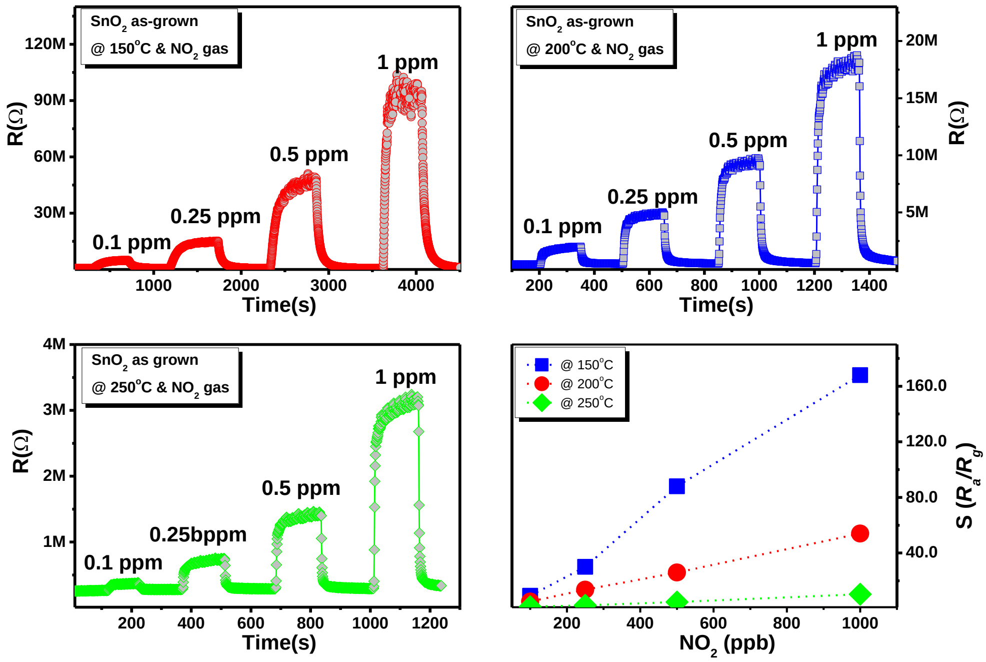


*Figure 3.* The $NO_2$ gas response of the as-growth $SnO_2$ at different temperatures:
(a) 250 °C, (b) 200 °C, (c) 150 °C and (d) The response with different gas concentration.

In this study, we investigated the effect of annealed temperature on gas sensor response. The $SnO_2$ nanowires were annealed at 400 °C, 500 °C and 600 °C in 5 hours and measured at operating temperature of 150, 200 and 250 $^oC$ and $NO_2$ gas concentrations of 100, 250, 500 and 1000 ppb $NO_2$ gas. The transient response of the three sensors was shown in Figure 4(a-c). Apparently, the annealed $SnO_2$ nanowire sensors exhibited a good response-recovery characteristic. The gas response as a function of gas concentration was shown in Figure 4(d-e). It can be seen clearly that the annealed temperature strongly depends on the gas response. In more details, the responses of the sensor annealed at 400, 500 and 600 °C upon exposure to 1000 ppb $NO_2$ at 200 $^oC$ are 68, 60 and 25, respectively. As compared with the as-grown $SnO_2$ nanowires, the sensors annealed at 400 and 500 $^oC$ have similar response. When annealed temperature increased up to 600 $^oC$, the response is significantly decreased. This could explain further study for plausible explanation.

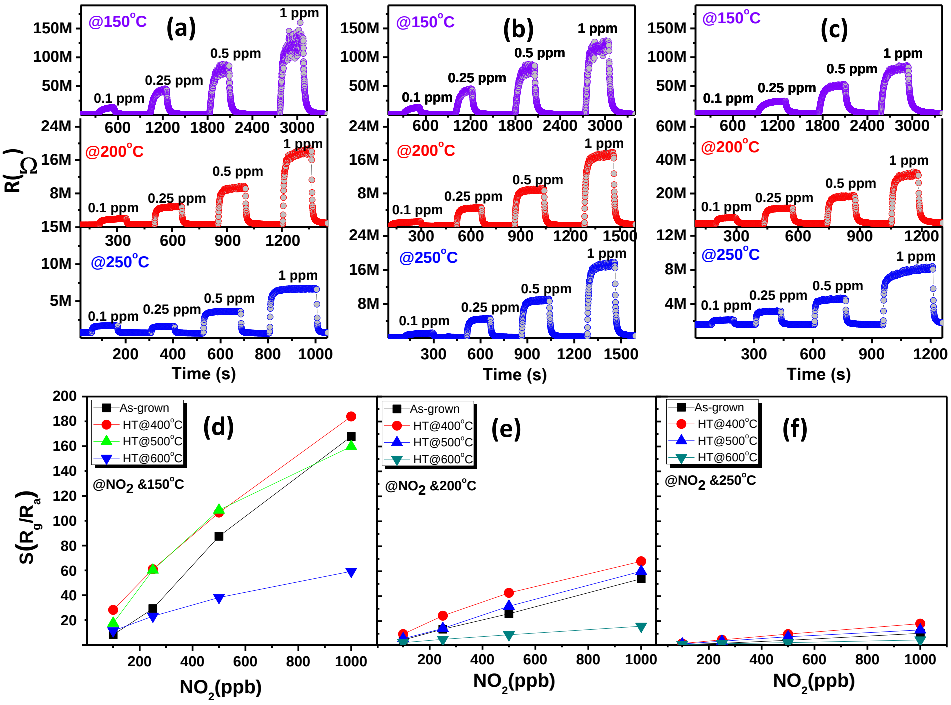

*Figure 4.* The transient response of $SnO_2$ nanowire sensors annealed at 400 °C (a), 500 °C (b) and 600 °C (c). The response as function of gas concentration measured at 200 °C (d), 150°C (e) and 250 °C (f).

The effect of source materials amount on gas sensing properties was shown in Figure 5. The results indicated that using 100 mg g of Sn powder to fabricate the on-chip sensor based on $SnO_2$ nanowires gave the highest response (around 25), while the sensor grown from 30 mg only gave the response of nearly 8 and the one grown from 150 mg had a response of about 13. Using 150 mg Sn powder resulted in a thicker layer of $SnO_2$ nanowires, thus making the adsorption of $NO_2$ onto the surface of the nanowires more difficult. In the case of using 30 mg source material, the as-grown layer was too thin, therefore the sensitivity was not as high as the sensor fabricated from 100 mg Sn powder.

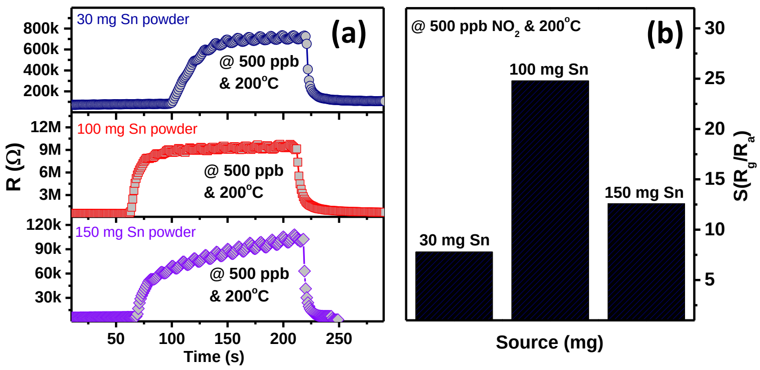


*Figure 6.* The transient response of $SnO_2$ nanowires grown from 30 mg (a), 100 mg (b) and 150 mg (c) Sn powder upon exposure to 500 ppb $NO_2$ at 200 °C and comparison response of the three sensors (d).

## 4. CONCLUSION

The $SnO_2$ nanowires were synthesized directly on the $Al_2O_3$ substrate equipped with electrodes by thermal evaporation route. This is a potential method that can be applied for mass-production of $SnO_2$ nanowire gas sensor. The $SnO_2$ nanowire sensor has exhibited good sensing performance to $NO_2$ gas. It can detect the concentration of $NO_2$ at ppb levels. Therefore, it is potential candidate to develop gas sensors for monitoring toxic and flammable gases.

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**TÓM TẮT**

ẢNH HƯỞNG CỦA NHIỆT ĐỘ Ủ ĐẾN TÍNH CHẤT NHẠY KHÍ $NO_2$
CỦA CẢM BIẾN DÂY NANO $SnO_2$

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Trong những năm gần đây tình trạng ô nhiễm môi trường do khí $NO_2$ sinh ra từ các phương tiện giao thông đang trở thành một vấn đề cấp bách, đặc biệt ở các thành phố lớn. Do đó, việc phát triển cảm biến khí $NO_2$ để kiểm soát chất lượng không khí đang thu hút được sự quan tâm nghiên cứu của các nhà khoa học trên thế giới. Trong nghiên cứu này, chúng tôi giới thiệu quy trình chế tạo dây nano $SnO_2$ bằng phương pháp bốc bay nhiệt từ bột Sn ở 750 $^oC$. Hình thái, cấu trúc và tính chất của vật liệu được khảo sát bằng nhiễu xạ điện tử tia X (XRD), hiển vi điện tử phát xạ trường (FE-SEM). Kết quả chế tạo vật liệu chỉ ra rằng, dây nano $SnO_2$ có đường kính khoảng 60 - 100 nm và chiều dài tới vài chục micro-mét. Tính chất nhạy khí $NO_2$ của cảm biến trên cơ sở dây nano $SnO_2$ xử lí nhiệt ở các nhiệt độ khác nhau cũng được khảo sát. Kết quả khảo sát cho thấy, khi xử lí nhiệt ở 400 $^oC$ và 500 $^oC$ không ảnh hưởng đến đặc trưng nhạy khí của cảm biến dây nano $SnO_2$. Tuy nhiên, khi xử lí ở nhiệt độ 600 $^oC$ làm suy giảm đáng kể độ đáp ứng của cảm biến với khí $NO_2$.

*Từ khóa*: $SnO_2$, $NO_2$, cảm biến khí, nhạy khí, dây nano.